

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : A61K 7/13	A1	(11) International Publication Number: WO 94/04125 (43) International Publication Date: 3 March 1994 (03.03.94)
(21) International Application Number: PCT/US93/07889 (22) International Filing Date: 23 August 1993 (23.08.93) (30) Priority data: 934,595 24 August 1992 (24.08.92) US (71) Applicant: REVLON CONSUMER PRODUCTS CORPORATION [US/US]; 625 Madison Avenue, New York, NY 10022 (US). (72) Inventors: GERSTEIN, Terry ; 12 Boston Post Road, East Brunswick, NJ 08816 (US). GOLDBERG, Marvin, E. ; 4 Palomino Way, Marlboro, NJ 07746 (US). (74) Agents: MISROCK, S., Leslie et al.; Pennie & Edmonds, 1155 Avenue of the Americas, New York, NY 10036 (US).		(81) Designated States: AU, BR, CA, JP, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: HAIR DYE PREPARATIONS AND ASSOCIATED METHODS		
(57) Abstract A hair dye composition comprised of a dye mixture, copper II catalyst-oxidizing agent, a surfactant, and water. A method for imparting permanent color to human hair comprising applying to the hair the composition of the invention.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi
BB	Barbados	GB	United Kingdom	NE	Niger
BE	Belgium	GN	Guinea	NL	Netherlands
BF	Burkina Faso	GR	Greece	NO	Norway
BG	Bulgaria	HU	Hungary	NZ	New Zealand
BJ	Benin	IE	Ireland	PL	Poland
BR	Brazil	IT	Italy	PT	Portugal
BY	Belarus	JP	Japan	RO	Romania
CA	Canada	KP	Democratic People's Republic of Korea	RU	Russian Federation
CF	Central African Republic	KR	Republic of Korea	SD	Sudan
CG	Congo	KZ	Kazakhstan	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovak Republic
CM	Cameroon	LU	Luxembourg	SN	Senegal
CN	China	LV	Latvia	TD	Chad
CS	Czechoslovakia	MC	Monaco	TC	Togo
CZ	Czech Republic	MG	Madagascar	UA	Ukraine
DE	Germany	ML	Mali	US	United States of America
DK	Denmark	MN	Mongolia	UZ	Uzbekistan
ES	Spain			VN	Viet Nam
FI	Finland				

- 1 -

HAIR DYE PREPARATIONS AND ASSOCIATED METHODSTechnical-Field

The invention is in the field of oxidation hair
5 dyes.

Background of the Invention

Man has been coloring his hair for more than 2000
years with various vegetable, mineral, and animal
substances which function as coloring agents. Today,
10 human hair dyes can generally be classified into one
of the following categories: oxidation dyes,
semipermanent dyes, temporary dyes, or miscellaneous.

The most important dyes for commercial hair
coloring are the oxidation dyes, which are also known
15 as "permanent" hair dyes, "permanent" meaning that the
hair color does not wash out with shampooing.

There are three components essential for
developing oxidation hair color shades:

1. Dye precursors (also known as primary
20 intermediates) and dye couplers (also known
as secondary intermediates) which condense
with the primary intermediates in the hair
fiber,
2. An oxidizing agent (usually hydrogen
25 peroxide); and
3. An alkaline pH.

Typically, the mixture of the dye precursors and
dye couplers in an alkaline vehicle is mixed with
hydrogen peroxide immediately prior to use. The
30 mixture is then applied to the hair and left on for a
specified period of time in order to allow the dye
molecules to penetrate into the hair shaft. The
hydrogen peroxide serves to oxidize the dye precursors
into large colored molecules. The dye couplers join
35 the reaction to modify the large molecules and their
color. These large colored molecules cannot be
extricated from the hair with normal shampoo

cleansing. The hair color is "permanent". The alkaline pH is important in this hair color process. The alkalinity helps swell the hair fiber to allow penetration of the initially small precursor dye
5 molecules. It activates the hydrogen peroxide which is supplied stabilized in acid media. It produces a suitable environment for the chemical reaction of the dyes with the hair.

A major disadvantage of most oxidative dye
10 systems is the employment of the hydrogen peroxide oxidizing agent which not only has the potential to damage the hair structure when used improperly, but also is known to cause other undesirable side effects such as skin irritation and burning in certain
15 sensitive individuals. Other oxidative dye systems have been developed which use peracid oxidizing agents, but these substances also present certain other problems. Recently, oxidative dye systems which rely on air oxidation have been developed. These
20 systems are commercially viable, although they tend to produce color development at a slow rate thus mandating that the dye mixture be left on the hair for extended periods of time.

It is most desirable to develop an oxidative hair
25 dye which provides quick, easy color to hair without using hydrogen peroxide or other undesirable oxidizing agents.

Summary of the Invention

30 The invention is directed to a dye composition comprising:

- (a) 0.0001-5% of a catalyst-oxidizing agent which is a copper II salt,
- (b) 0.001-5% of a dye blend comprised of primary
35 intermediates and couplers,
- (c) 0.1-70% water,
- (d) 0.01-60% surfactant.

The invention is also directed to a method for imparting permanent color to human hair comprising applying to the hair the above mentioned composition.

5 Detailed Description

The copper II salts (or "copper II catalyst-oxidizing agents") in accordance with the invention include copper II sulfate, copper II chloride, copper II oleate, copper II pyridinethione, copper II
10 acetate, copper II phosphate, copper II gluconate, copper II glycinate, copper II stearate, etc., or mixtures thereof. Preferred are copper II sulfate and copper II chloride.

The term "dye blend" means the combination of dye
15 intermediates used for producing color.

The term "dye mixture" means the component of the invention containing the dye blend in a vehicle formulated with other ingredients such as solvents, surfactants, conditioning agents, stabilizers, etc.

20 The term "dye composition" means the dye mixture together with the catalyst-oxidizing agent.

The following are suitable primary intermediates, and in parentheses following each intermediate is the color it imparts to hair: p-phenylenediamine (dark
25 brown/black), 2,5-diaminotoluene (reddish brown), 2-chloro-p-phenylenediamine (brown), N-phenyl-p-phenylenediamine (dark gray/black), N,N-bis-(2-hydroxyethyl)-p-phenylenediamine (brown), p-aminophenol (light auburn), N-methyl-p-aminophenol
30 (pale blond), or mixtures thereof.

Suitable dye couplers are resorcinol, 4-chlororesorcinol, 2-methylresorcinol, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 2,5-dihydroxypyridine, m-aminophenol, 4-methyl-5-
35 aminophenol, 4-methyl-5-(2-hydroxyethyl)aminophenol, m-phenylenediamine, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, o-aminophenol, or mixtures thereof.

As is understood by those skilled in this art, the total combination of particular couplers and primary intermediates used vary with the intended shade of hair color desired.

5 The dye composition of the invention may be administered to hair in a number of different product modes. The traditional manner is preferred, wherein the hair dye blend in a surfactant vehicle together with the copper II catalyst-oxidizing agent are
10 applied to the hair for a specified period of time and color is allowed to develop before the dye composition is removed from the hair. In the case of the invention, the dye couplers and intermediates found in the dye mixture are small molecules which are able to
15 penetrate the hair shaft. The copper II catalyst-oxidizing agent initiates reaction of the dye molecules which causes the molecules to complex to form larger polymers within the hair shaft. The complexed molecules become too large to escape from
20 the hair shaft and permanent color is thus obtained.

Suitable hair dye compositions in accordance with the invention comprise 0.0001-5% of the copper II catalyst-oxidizing agent as set forth herein, 0.001-5% of the dye blend, 0.01-30% surfactant, 0.01-10%
25 conditioners, 30-70% water. In the preferred embodiment of the invention, the copper II catalyst-oxidizing agent is copper sulfate or copper chloride.

The surfactants which are suitable in the composition of the invention may be anionic, cationic,
30 nonionic, or amphoteric. Suitable anionic surfactants include fatty acid soaps, salts of alkyl sulfates, salts of alkyl ether sulfates, N-acyl sarcosinates, salts of fatty acid amide sulfonic acids, salts and/or esters of alkyl phosphates, salts of fatty
35 sulfosuccinates, alkyl benzene sulfonate salts, salts of N-acyl glutamate, salts of fatty sulfoacetates, alpha olefin sulfonate salts, or mixtures thereof.

The amphoteric surfactants which are useful in the compositions of the present invention may be ampholytic or zwitterionic and include betaines, sultaines, imidazolines, phosphobetaines, phosphitaines and pyrophosphobetaines, and also include glycinates, beta amino propionates, and other surface active amino acid derivatives.

Suitable-cationic surfactants include halogen and sulfate salts such as benzalkonium chloride, stearylalkonium chloride, laurtrimonium chloride, cetrimonium chloride., soytrimonium chloride, stearyltrimonium chloride, dicocodimonium chloride, quaternium 18, distearyldimonium chloride, tallowdimonium propyltrimonium dichloride, tricetylmonium chloride, PEG-2 cocomonium chloride, PEG-2 oleamonium chloride, PEG-15 stearamonium chloride, as well as pyridinium, morpholinium, imidazolinium salts, and various salts of long chain primary, secondary, and tertiary amines.

Both lipophilic and hydrophilic nonionic surfactants are suggested, such as sorbitan fatty acid esters, alkyl ether glycosides, ethoxylated/propoxylated long chain alcohols, and acids, ethoxylates of long chain mono and diglycerides, long chain amine oxides, alkanolamides, lanolin derived ethoxylates and so on.

Employable surfactants in accordance with the invention are salts of isostearic acid and oleic acid, PEG-2 cocoamine, cetareth-4- phosphate, sulfated castor oil, nonoxynol-1, PEG-5 oleate, cetareth-10, cocobetaine, sodium lauryl sulfate, ammonium laureth sulfate, ammonium lauroyl sarcosinate, stearamine oxide, cetrimonium chloride, cocoamidopropyl betaine, behenyl dimethylamine hydrochloride, nonoxynol-121 potassium coco-hydrolyzed animal protein, sodium cocoyl isethionate, polyglyceryl-4-stearate, PPG-8-ceteth-10, sodium cocoyl glutamate, caprylyl/capryl

glucoside, sodium cocamphoacetate, cocosultaine, stearalkonium chloride, cetareth-15, lauramide DEA, stearamidopropyldimethylamine hydrochloride, dicetyldimonium chloride, C₁₁₋₁₅ pareth-20 and others of
5 the like.

Suitable auxiliary ingredients which also provide conditioning effects include hydrolyzed animal/vegetable protein, propylene glycol, sorbitol, PPG-40 butyl ether, stearic acid, panthenol, vitamin E
10 palmitate, dimethicone, propylene glycol monostearate, ethylene glycol distearate, amodimethicone, dimethiconol, dimethicone copolyol, ethylene glycol stearate, isopropyl myristate, cetyl lactate, cetearyl alcohol, cetyl alcohol, butylene glycol, aloe vera
15 gel, acetamide MEA, oleyl alcohol, cyclomethicone, decyl oleate, mineral oil, lanolin alcohol or mixtures thereof.

When the dye mixture and the copper II catalyst-oxidizing agent are combined together and administered
20 to the hair in the form of a dye composition, the composition is left on the hair for an appropriate period of time, generally 5-45 minutes. The hair is then rinsed with water and dried. If desired, the hair may be treated in a two step process with the dye
25 mixture first, then removed, then followed by post-dye hair treatment products which contain the copper II catalyst-oxidizing agent. Application of such post-treatment products containing copper II will act to oxidize unreacted dye molecules within the hair shaft,
30 causing color development instantly.

The dye composition of the invention can also be administered in the form of mousse, which when regularly used will result in more intense color development with each subsequent treatment. A
35 suitable mousse composition comprises 0.1-20% of a hair fixative, 0.01-20% surfactant, 0.01-10% thickeners, 0.001-5% dye blend, 0.0001-5% copper II

catalyst-oxidizing agent, 30-70% water, and 25-75% solvent. This composition is then mixed with a suitable propellant. Generally 70-98 parts of the above composition and about 2-30 parts of propellant
5 are suitable. Suitable propellants include dimethyl ether, n-butane, isobutane, difluoroethane, chlorodifluoroethane, chlorodifluoromethane, other chlorofluorocarbons, or mixtures thereof.

As stated previously, in accordance with the
10 invention, it is possible for the dye mixture to be administered to the hair first, followed by the application of a second vehicle which contains the copper II catalyst-oxidizing agent. In this instance, the dye mixture in the form of a lotion, creme,
15 shampoo or alternative vehicle is initially applied to the hair and allowed to remain for a period of time long enough to ensure that the dye molecules penetrate the hair shaft. The dye mixture is then rinsed out of the hair. A second composition, such as a shampoo,
20 conditioner, or treatment product which acts as a vehicle for the copper II catalyst-oxidizing agent is then applied to the hair. After an appropriate period of time relative to the nature of the composition, it is washed out of the hair. Hair is left colored
25 instantly to a new shade.

Hair which has been colored according to the invention, can be subsequently maintained with the application of various post-dye conditioning products such is shampoos, spritzers, hair sprays,
30 conditioners, and the like. These products contain the copper II catalyst-oxidizing agent which act to ensure total and prolonged color intensification and stabilization.

Such a suitable shampoo useful as a post-dye
35 treatment product includes 10-60% anionic, amphoteric, or betaine surfactants or mixtures thereof, 0.01-15% conditioners, 0.01-5% thickener, and 0.0001-5% copper

II oxidizing agent. The shampoo composition may additionally contain 0.01-10% silicone such as dimethicone, dimethicone copolyol, amodimethicone, cyclomethicone or mixtures thereof. It may also be
5 desired to add 0.1-5% antidandruff ingredients such as selenium sulfide, zinc pyridinethione, copper II pyridinethione, etc. Use of such a shampoo composition after hair has been dyed in accordance with the invention may result in a gradual color
10 enhancement of the hair until all of the unreacted dye molecules have been activated.

Another good post-dye treatment vehicle is a creme rinse. Suitable creme rinse formulations comprise 0.01-10% of a cationic surfactant, 0.01-20%
15 conditioners, 0.001-5% thickening agents, 0.0001-5% copper II oxidizing agent, and the remainder water. Suitable cationic surfactants include stearylalkonium chloride, cetrimonium chloride, dicetyl dimonium chloride, or mixtures thereof. Suitable conditioners
20 are many, and include cetearyl alcohol, cetyl alcohol, panthenol, aloe vera gel, dimethicone, dimethicone copolygl, amodimethicone, ceteareth, hydrolyzed vegetable proteins, oleyl aldohol, cyclomethicone, lanolin, mineral oil, lanolin alcohol, or mixtures
25 thereof.

Aerosol hair sprays or pump hair sprays may also act as a post-dye treatment vehicle. Suitable hair spray formulations comprise 0.01-10% hair fixative resin, 0.001-10% conditioner, 25-90% organic or
30 aqueous solvent, 0.0001-5% copper II oxidizing agent. The hair spray may also contain 0.001-5% fragrance, as well as other constituents. If the hair spray is an aerosol, generally about 50-90 parts of the hair spray mixture is combined with 10-50 parts of propellant as
35 set forth herein. If the hair spray composition is used in a pump spray it is generally desired to include about 0.01-45% water.

Suitable hair fixative polymers include acrylate/acrylamide copolymer, esters of polyvinyl methyl ether/maleic anhydride (PVM/MA) copolymer, octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, octylacrylamide/acrylates copolymer, polyquaternium-4, polyquaternium-7, polyquaternium-10, polyquaternium-11, polyvinyl pyrrolidone (PVP), polyvinyl pyrrolidone vinyl acetate (PVP/VA) copolymer, shellac, vinyl acetate/crotonic acid copolymer, vinyl acetate/crotonic acid/vinyl neodecanoate copolymer, and so on.

Hair styling gels may also be suitable for post-dye treatment vehicles. Suitable hair gels comprise 0.001-10% hair fixative resin, 0.01-15% conditioner, 30-70% solvent, 30-70% water, and 0.0001-5% copper II catalyst-oxidizing agent.

The invention is directed to a method for imparting permanent color to human hair comprising applying to the hair an oxidizing agent selected from the group consisting of copper II sulfate, copper II chloride, copper II oleate, copper II pyridinethione, copper II acetate, copper II phosphate, copper II gluconate, copper II glycinate, copper II stearate, or mixtures thereof; and a dye mixture comprised of a primary intermediate and a coupler wherein the primary intermediate is selected from the group consisting of p-phenylenediamine, 2,5-diaminotoluene, 2-chloro-p-phenylenediamine, N-phenyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, p-aminophenol, N-methyl-p-aminophenol, or mixtures thereof; and the couplers from the group resorcinol, 4-chlororesorcinol, 2-methylresorcinol, 1-naphthol, 1,5-dihydroxynaphthalene, 1,7-dihydrozynaphthalene, 2,5-dihydroxypyridine, m-aminophenol, 4-methyl-5-aminophenol, 4-methyl-5-(2-hydroxyethyl)aminophenol, m-phenylenediamine, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, o-aminophenol, or mixtures thereof.

In the preferred embodiment of the invention, a composition containing both the dye mixture and the copper II catalyst-oxidizing agent is applied to the hair and allowed to remain for 5-45 minutes. The composition is then rinsed from the hair and the hair is towel dried. The hair is left colorized to a new shade. If desired, various post-dye treatment maintenance products containing the catalyst-oxidizing agent may be used on a regular basis in order to cause any unaffected dye molecules to colorize. The hair color will continue to gradually intensify until all of the dye molecules have reacted within the hair shaft.

It may be desired to color the hair in a two step process wherein the dye mixture is applied to the hair via the appropriate vehicle. After the dye mixture is removed, a second composition containing the copper II catalyst-oxidizing agent is applied. After rinsing again, the hair is left colored to a new shade. Suitable vehicles to hold the catalyst-oxidizing agent for a two step process include shampoo, conditioner, etc.

In this case too it may also be desired to routinely use maintenance hair products such as mousse, shampoo, or the like wherein the catalyst-copper II oxidizing agent is incorporated directly into the product. Again, regular use of the product results in a maximum hair color development and stabilization over time.

The compositions and methods of the invention provide an excellent method for coloring human hair without the use of hydrogen peroxide. The methods and compositions of the invention are particularly useful in coloring gray hair.

The invention will be further described in connection with the following examples which are set forth for the purposes of illustration only.

Example 1

A hair dye composition suitable for a one step treatment in accordance with the invention is shown as follows:

5		<u>w/w%</u>
	Isostearic acid	22.0
	Oleamide DEA	10.0
	TEA Coco hydrolyzed animal protein	4.0
	Ethanolamine	12.0
10	Oleth-15	1.0
	Hydrolyzed animal protein	0.5
	Propylene glycol	7.0
	Dye blend	2.0
	Copper II sulfate	0.1
15	Fragrance, stabilizer	QS
	Water	QS 100.

The above composition was applied directly to dry hair and worked into a creamy rich lather with the fingertips so that hair was thoroughly saturated. The product was left on the hair for 25 minutes. Then, a small amount of water was added and the lather worked up before rinsing out with water. After the composition has been completely removed, the hair is washed with a standard conditioning shampoo. The hair is left colored to another shade. If desired, the hair can be routinely shampooed with the post-treatment shampoos taught herein.

Example 2

A hair dye composition suitable for one step treatment in accordance with the invention was made as follows:

		<u>w/w%</u>
	K Coco hydrolyzed animal protein	5.0
	Oleic acid	18.5
35	Linoleamide DEA	5.0
	Isopropanol	4.7
	PPG-40 Butyl ether	0.2

	Ethanolamine	9.0
	TEA Lauryl sulfate (40%)	5.0
	Oleamide DEA	5.0
	PEG-2 Cocamine	2.5
5	Sodium EDTA	0.3
	Laneth-5	0.8
	Sodium sulfite	1.0
	Erythorbic acid	0.1
	Copper II chloride	1.0
10	Dye mixture	QS to shade
	Water	QS 100.0

The composition is applied in accordance with the method set forth in Example 1.

15 Example 3

A dye composition suitable for a one step treatment is shown in accordance with the following formula:

	<u>w/w%</u>
20	Dye mixture
	1.0
	Oleic acid
	15.0
	Propylene glycol
	8.0
	Panthenol
	1.0
	Isopropanol
	9.0
25	Octoxynol-1
	7.0
	Sulfated castor oil
	3.0
	Ammonium hydroxide (28%)
	8.2
	Lauramide DEA
	1.5
	Copper II sulfate
	1.5
30	Fragrance, stabilizer
	QS
	Water
	QS 100.0

The composition is applied in accordance with the method of Example 1.

35

Example 4

A hair dye composition with cationic conditioning agent suitable for a one step treatment is shown as follows:

5		<u>w/w%</u>
	Oleamide DEA	2.0
	Isostearamide DEA	3.0
	Ethanolamine hydrochloride	22.0
	Ethyoxydiglycol	5.0
10	Hexylene glycol	3.0
	Nonozynol-1	18.0
	Isopropanol	13.0
	Soyatrimethyl ammonium chloride	3.0
	Dye mixture	2.0
15	Copper II sulfate	2.5
	Stabilizer, fragrance, preservative	QS
	Water	QS 100.0

The composition is applied to dry hair or to hair which has just been shampooed. The composition is
20 allowed to remain on hair for approximately 25 minutes before being washed off.

Example 5

A hair styling mousse for gradual color
25 development is shown as follows:

		<u>w/w%</u>
	Polyquaternium-11 (20%)	12.25
	Stearalkonium chloride	0.18
	Djmethicone	0.05
30	Ethanol	40.00
	Triethanolamine	0.80
	PEG-5 Oleate	0.44
	Ceteareth-.10	0.15
	Fragrance	0.05
35	Sodium sulfite	0.08
	p-Phenylenediamine	0.20
	4-Chlororesorciol	0.005

p-Aminophenol	0.005
Copper II sulfate	0.005
Water	QS 100.00

The mousse was obtained by mixing 92 parts of the
5 above concentrate with 8 parts of Propellant 152A
(E.I. Dupont de Nemours, Inc., Wilmington DE), and
dispensed with aerosol packaging. The mousse is
applied to hair and evenly worked through with the
fingers. The hair is styled as usual.

10 Alternatively, the mousse may be used in the
manner of a shampoo. In this case, the mousse is
liberally applied to the hair, worked in, and allowed
to remain for 10-30 minutes before washing out.
Examples 6, 7, and 8 show rinse-out hair color mousse
15 compositions.

Example 6

A conditioning mousse composition is shown by
combining 90 parts by weight of the dye composition of
Example 2 with 10 parts by weight of Propellant 152A.
20

Example 7

A panthenol mousse composition is shown by
combining 92.0 parts by weight of the dye composition
of Example 3 with 8.0 parts by weight of Propellant
25 152A.

Example 8

A mousse with cationic conditioner was made by
combining 92.0 parts by weight of the dye composition
30 of Example 4 with 8.0 parts by weight of Propellant
152A.

Example 9

A high foaming shampoo useful as a post-treatment
35 color development product is shown as follows:

	<u>w/w%</u>
Sodium lauryl sulfate (28%)	25.0

	Sodium laureth sulfate (28%)	35.0
	Coco betaine (30%)	3.3
	Cocamide DEA	2.0
	Copper II chloride	2.5
5	Buffer solution	QS to pH 6.0
	Hydroxypropylmethylcellulose	0.8
	Hydrolyzed vegetable protein	0.5
	Water	QS 100.0

Hair has been previously treated with the dye mixture vehicle in accordance with the invention is cleansed with the above shampoo. Hair color will develop due to activation of the dye molecules which have penetrated the hair fiber.

15 Example 10

A mild shampoo useful as a post-treatment color development product is shown as follows:

		<u>w/w%</u>
	Ammonium laureth sulfate (28%)	30.0
20	Lauroyl sarcosine	5.0
	Lauramide DEA	2.0
	Stearamine oxide (25%)	4.0
	Hydroxyethyl cellulose	1.0
	Copper II sulfate	0.5
25	Ethylene glycol stearate	1.0
	Stabilizer, fragrance, color	QS
	Water	QS 100.0

30 Example 11

Two in one shampoo conditioner useful for a post-treatment color development product is shown as follows:

		<u>w/w%</u>
	Ammonium lauryl sulfate (28%)	35.0
35	Ammonium laureth sulfate (28%)	20.0
	Dimethiconol	0.5
	Amodimethicone	0.8

	Cetrimonium chloride	0.3
	Cocoamidopropyl betaine (37%)	4.0
	Methyl cellulose	1.0
	Behenyldimethylamine hydrochlorid	3.0
5	Copper II chloride	1.0
	Copper II oleate	1.0
	Fragrance, color, stabilizer	QS
	Water	QS 100.0

10 Example 12

A mild amphoteric shampoo suitable for a post-treatment color development product is shown as follows:

		<u>w/w%</u>
15	Copper II glycinate	2.0
	Sodium cocoyl glutamate	0.1
	Caprylyl/capryl glucoside (60%)	20.0
	Sodium cocoamphoadetate (43%)	20.0
	Cocoyl sarcosine	2.35
20	Copper II chloride	0.5
	Acrylates/steareth-20 methacrylate copolymer	6.67
	Fragrance, stabilizer, preservative, color	QS
	Water	QS 100.00

25

Example 13

A conditioning shampoo suitable as a post-treatment color development product is shown as follows:

		<u>w/w%</u>
30	Amonium lauryl sulfate (28%)	40.0
	Cationic guar gum	0.2
	Cocamidopropyl betaine (37%)	4.5
	Dimethicone copolyol	2.0
35	Ethylene glycol stearate	1.5
	Myristamide DEA	1.0
	Copper II sulfate	5.0

Fragrance, stabilizer	QS
Water	QS 100.0

Example 14

- 5 A dandruff rinse shampoo suitable as a post-treatment color development product is shown as follows:

	<u>w/w%</u>
Sodium lauryl sulfate (28%)	50.0
10 Lauramine Oxide (25%)	8.0
Copper II pyridinethione	0.5
Copper II sulfate	0.8
Di(hydrogenated) tallow phthalic acid amide	5.0
15 Copper II citrate	0.2
Fragrance, stabilizer	QS
Water	QS 100.0

Example 15

- 20 A creme rinse suitable as a post-treatment color development product is shown as follows:

	<u>w/w%</u>
Stearalkonium chloride	2.8
Cetearyl alcohol	1.0
25 Ceteareth-15	1.5
Hydroxyethyl cellulose	1.0
Copper II sulfate	5.0
Fragrance, stabilizer	QS
Water	QS 100.0

30

Example 16

- An extra conditioning conditioner suitable as a post-treatment color development product is shown as follows:

	<u>w/w%</u>
35 Cetrimonium chloride	1.5
Cetearyl alcohol	1.5

	Ceteareth-20	2.5
	Stearamidopropyldimethylamine hydrochloride	2.5
	Cetyl alcohol	0.5
5	Copper II acetate	0.1
	Copper II chloride	2.5
	Hydrolyzed wheat protein	0.5
	Hydroxyethyl cellulose	0.5
	Panthenol	0.25
10	Water	QS 100.00
	Fragrance, stabilizer	QS

Example 16

15 An extra body conditioner suitable for use as a
post-treatment color development product is shown as
follows:

		<u>w/w%</u>
	Dicetyldimonium chloride	2.0
	Aloe vera gel	3.0
20	Acetamide MEA	0.7
	Cetyl alcohol	0.8
	Ceteareth-15	2.0
	Polyquaternium-4	1.0
	Copper II nitrate	0.01
25	Cooper II citrate	0.2
	Copper oleate	0.2
	Dimethicone copolyol	0.5
	Preservatiye, fragrance, color	QS
	Water	QS 100.0

30

Example 17

A rinse off conditioner for ulotrichous hair
suitable for use as a post-treatment color development
product is shown as follows:

35		<u>w/w%</u>
	Stearalkonium chloride	1.5
	Cetrimonium chloride	1.5

	Amodimethicone	1.0
	Cetearyl alcohol	0.9
	Ceteareth-6	0.9
	Ceteareth-20	1.5
5	Hydrolyzed legume protein	1.7
	Copper II sulfate	1.0
	Preservative, fragrance, color	QS
	Water	QS 100.0

10

Example 18

A post-dye composition treatment product in the form of a hair thickening aerosol hair spray is shown in accordance with the following formula. The hair spray was intended to be applied after a dye

15 composition treatment to sustain longevity of the hair color as well as to intensify the hue with time:

		<u>W/W%</u>
	PVP	2.0
	PVP-VA	4.0
20	Copper II Phosphate, fine	0.0001
	Copper II Sulfate	0.01
	Oleyl alcohol	0.3
	Cyclomethicone	0.2
	Benzophenone-3	0.3
25	Water	15.5
	Fragrance	0.1
	Ethanol	47.48
	Propellant blend	30.00

30

Example 19

A post-dye composition treatment hair styling gel is shown as follows:

		<u>W/W%</u>
35	Acrylates/C ₁₀ -C ₃₀ alkylacrylates crosspolymer	1.0
	PVP	3.5
	Copper II gluconate	0.01

	Copper II chloride	0.01
	Sodium hydroxide	0.3
	Propylene glycol	0.5
	Fragrance	QS
5	Ethanol/water (50/50)	QS 100.0

Example 20

A post-dye composition treatment pump spritz spray is shown as follows:

10		<u>w/w%</u>
	Octylacrylamide/acrylates/butylamino-ethyl methacrylate copolymer	5.0
	Aminoethylpropanol	0.9
	Copper II citrate	0.2
15	Copper II sulfate	0.01
	Lauramide DEA	0.5
	Cyclomethicon	0.1
	Benzophenone-4	0.1
	Fragrance	QS
20	Water	13.0
	Ethanol	QS 100.0

Example 21

A post-dye treatment sheen hair dressing is shown as follows:

25		<u>w/w%</u>
	Ethoxylated lanolin alcohol	3.0
	Oleth-10	10.0
	Mineral oil and lanolin alcohol	10.0
30	Ceteth-10	5.0
	Copper II stearate	1.0
	Propylene glycol	5.0
	Copper II oleate	0.1
	Copper II sulfate	0.1
35	Decyl oleate	4.0
	Preservative, fragrance, stabilizer	QS
	Water	QS 100.00

Example 22

A post-dye composition treatment hair setting mousse concentrate is shown as follows:

	w/w%
5 Quaternium-11 (20%)	2.0
PVP-VA (50%)	6.0
Steareth-2	0.5
Dimethicone copolyol	0.2
Nonoxynol 12	0.3
10 Cetrimonium chloride	0.5
Hydrolyzed vegetable protein	0.1
Polysorbate 20	0.4
Copper II sulfate	0.08
Fragrance, stabilizer	QS
15 Water	QS 100.00

Ninety parts of the above concentrate was mixed with 10 parts of Propellant 152A.

Example 23

- 20 A mousse composition was prepared by mixing 90 parts of Revlon Colorsilk Brown Hair dye which contained 1% cupric chloride, with 10 parts of Dymel 152A. Hair tresses were treated for 15 minutes each in four intervals. The tresses turned more intense
- 25 brown after each treatment. Maximum color development occurred after 45 minutes (3 treatments). A two week control mousse stored at 120° F for aging effects did not show any color differences when tested against the mousse composition stored at room temperature.
- 30 A separate set of hair tresses were treated with Revlon Colorsilk Black Indigo dye in the directed manner for 20 minutes, but without the addition of hydrogen peroxide developer. Hair tresses were removed from the bath, the dye was rinsed off, and the
- 35 tresses shampooed with Revlon Nintendo shampoo. One hair tress was dipped into hydrogen peroxide developer, another dipped into 3% Na₂SO₃ solution. A

third tress was dried as is. The hair tress dipped into developer turned deep black. The hair tress treated-with 3% Na_2SO_3 turned slightly colored with time. Hair with no further treatment turned only
5 nominally in color and slowly intensified over a prolonged interval of time.

CONCLUSION: Dye penetrates into hair and will not wash out. It can be reacted at a subsequent time by either oxygen in air or hydrogen peroxide. Sodium
10 sulfite solution slightly inhibits the oxidation effects of air at the concentration used.

Further, 95% gray hair tresses were treated with Revlon Colorsilk Black Indigo dye for 20 minutes. The tresses were rinsed out with water, shampooed with
15 Revlon Nintendo shampoo, and towel dried. The tresses were further treated as follows: (1) 3% Na_2SO_3 solution, (2) 0.5% CuCl solution, (3) 5.0% CuCl_2 solution, (4) 6% solution of hydrogen peroxide.

Results: (1) left hair slightly smokey looking.
20 (2) left hair deep gray. (3) left hair deep gray-black (4) left hair looking midway between #2 and #3.

CONCLUSION: CuCl_2 behaves similarly to H_2O_2 in post dye treatment effects to produce hair color with oxidation dyes.
25

30

35

WHAT IS CLAIMED IS:

1. A composition capable of imparting permanent
5 color to human hair comprising:
 - (a) 0.0001-5% of an oxidizing agent which is a copper II salt,
 - (b) 0.001-5% of a dye comprised of a primary intermediate and a coupler,
 - 10 (c) 0.01-70% water,
 - (d) 0.01-60% surfactant.
2. The composition of claim 1 wherein the copper II salt is selected from the group consisting of copper II sulfate, copper II chloride, copper II
15 oleate, copper II pyridinethione, copper II acetate, copper II phosphate, copper II gluconate, copper II glycinate, copper II stearate, etc., or mixtures thereof.
3. The composition of claim 2 wherein the
20 primary intermediate is selected from the group consisting of p-phenylenediamine, 2,5-diaminotoluene, 2-chloro-p-phenylenediamine, N-phenyl-p-phenylenediamine, N,N-bis-(2-hydroxyethyl)-p-phenylenediamine, p-aminophenol, N-methyl-p-
25 aminophenol, or mixtures thereof.
4. The composition of claim 3 wherein the coupler is selected from the group consisting of resorcinol, 4-chlororesorcinol, 2-methylresorcinol, 1-naphthol, 1,5-dihydroxynaphthalene,
30 1,7-dihydroxynaphthalene, 2,5-dihydroxypyridine, m-aminophenol, 4-methyl-5-aminophenol, 4-methyl-5-(2-hydroxyethyl)aminophenol, m-phenylenediamine, 2,4-diaminophenoxyethanol, 2,6-diaminopyridine, o-aminophenol, or mixtures thereof.

35

5. The composition of claim 4 wherein the surfactant is an anionic, cationic, nonionic, or amphoteric surfactant.

5 6. The composition of claim 5 wherein the surfactant is selected from the group consisting of isostearic acid, TEA coco hydrolyzed animal protein, oleth-15, oleic acid, PEG-2 cocoamine, octoxynol-1, sulfated castor oil, nonoxynol-1, stearalkonium
10 chloride, PEG-5 oleate, ceteareth-10, cocobetaine, sodium lauryl sulfate, sodium laureth sulfate, ammonium laureth sulfate, lauroyl sarcosine, stearamine oxide, cetrimonium chloride, cocoamidopropyl betaine, behenyl dimethylamine
15 hydrochloride, sodium cocoyl glutamate, caprylyl/capryl glucoside, sodium cocamphoacetate, ammonium lauryl sulfate, stearalkonium chloride, ceteareth-15, ceteareth-20, stearamidopropyldimethylamine hydrochloride,
20 dicetyldimonium chloride, cetearyl alcohol, ceteareth-6, or mixtures thereof.

7. The composition of claim 6 additionally comprising 0.01-10% conditioners.

8. The composition of claim 7 additionally
25 comprising 0.1-20% hair fixative, 0.01-10% thickener and 25-75% solvent.

9. The composition of claim 8 additionally comprising a propellant.

10. A method for imparting permanent color to
30 human hair comprising applying to the hair a copper II salt and a dye mixture comprised of a primary intermediate and a coupler.

11. The method of claim 10 wherein the copper II salt and dye mixture are simultaneously applied in a
35 single composition.

12. The method of claim 11 wherein the dye mixture is applied in a first step and the copper II salt is applied in a second step.

13. The method of claim 11 wherein the hair is
5 treated/maintained with a post-treatment product containing copper II salt.

14. The method of claim 11 wherein the single composition comprises a hair dye composition or a mousse composition.

10 15. The method of claim 13 wherein the post treatment product is selected from the group consisting of shampoo, hair spray, hair spritzer, styling gel, or creme rinse.

15

20

25

30

35

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US93/07889

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :A61K 7/13

US CL :8/406, 405, 408, 416, 421, 435

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 8/406, 405, 407, 408, 416, 421, 435; 424/70

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US, A, 4,992,077 (Tennigkeit et al) 12 February 1991, See Abstract and Examples 1a, 1b, 3a, 3b.	<u>1-8, 10-12, 14</u> 1-15
X,P Y	US, A, 5,199,954 (Schultz et al) 06 April 1993, See col. 2, lines 29-61; col. 4, lines 62-68; col. 6, lines 37-68.	<u>1-3, 10-15</u> 1-15
A	US, A, 3,981,677 (Halasz et al) 21 September 1976, See Abstract; col. 4, lines 50-53.	9
A	US, A, 5,112,359 (Murphy et al) 12 May 1992, See col. 4, lines 27-52.	9
A,P	US, A, 5,173,085 (Brown et al) 22 December 1992, See col. 2, lines 41-59.	1-2, 10-12

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to underpin the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, each combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

18 OCTOBER 1993

Date of mailing of the international search report

22 NOV 1993

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. NOT APPLICABLE

Authorized officer

PAUL LIEBERMANN

Telephone No. (703) 308-2523